Towards Fuel Efficient DPF Systems: Understanding the Soot Oxidation Process

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Background: Active DPF Applications

- Accurate mathematical understanding of the soot oxidation process is critical for active DPF systems
  - Robust design, based on the fundamental understanding of the regeneration process
  - Active Controls: virtual soot sensors

$$\boxed{m_{soot} = \int \dot{m}_{generation}\,dt - \int \dot{m}_{oxidation}\,dt}$$

$$\boxed{\dot{m}_{oxidation} = f\,(T, [O_2], [H_2O], [NO_2], [CO_2], \text{soot properties})}$$

- Significance:
  - Quantitative approach to the key application / controls trade-offs, for example:

Risk of DPF failure

Fuel Penalty

Regeneration efficiency (frequency, duration, target temperature)

Application optimization opportunities

What do we need to know about soot oxidation to develop optimal and safe regeneration strategies?

I. Mechanisms of soot oxidation by NO_2 and by O_2

II. Soot properties, including their evolution with oxidation

III. Effects of various catalytic technologies

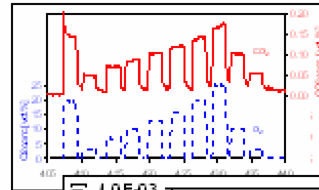
IV. Soot deposition topology

I. Soot oxidation mechanism:

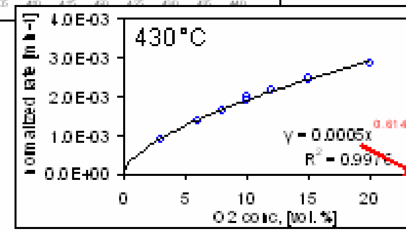
Cummins Program

- Novel methodology[1,2]
  - Resolved major experimental limitations
  - Statistic analysis-capable data
  - Complete kinetic analysis at any soot oxidation “age”

Example – Effect of O_2 concentration



Multiple O_2 sweeps
- T = 405-553°C
- $[O_2]$ = 3-25 vol. %
- C conversion = 15-77%



sample #	Series	T, °C	Soot conv. % Beginning of the series	End of the series	Order	R^2
1	1	405	14.2	15.1	0.66	0.998
1	2	454	15.7	18.6	0.67	0.980
1	3	504	20.6	31.3	0.68	0.996
1	4	529	33.4	43.5	0.60	0.973
1	5	479	44.1	48.1	0.68	0.998
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	7	553	51.6	67.3	0.68	0.971
1	8	455	71.0	72.6	0.61	0.996
2	9	461	24.5	28.2	0.66	0.998
2	10	535	28.5	49.1	0.68	0.963
2	11	510	50.3	59.2	0.60	0.998
2	12	485	59.8	63.5	0.61	0.998
2	13	461	63.5	65.3	0.67	0.998
2	14	510	69.0	74.5	0.62	0.993
2	15	485	74.8	77.3	0.68	0.996
2	16	461	77.4	79.5	0.66	0.999
				average order	0.61	
				standard deviation	0.03	

- Statistics-capable data
  - Confidence intervals

- Comprehensive kinetic description of the O_2-soot oxidation process (key contributor to active regeneration)
  - Fundamentally-based equation, hence platform-independent and capable of extrapolation
  - Mathematically uncomplicated: can be implemented in engine ECMs

[1] A.Yezerets, N.W.Currier, H. Eadler. SAE 2003-01-0833
[2] A. Yezerets, et al. Applied Catalysis B: 61 (2005), p134

II. Impact of Soot Properties on Reactivity

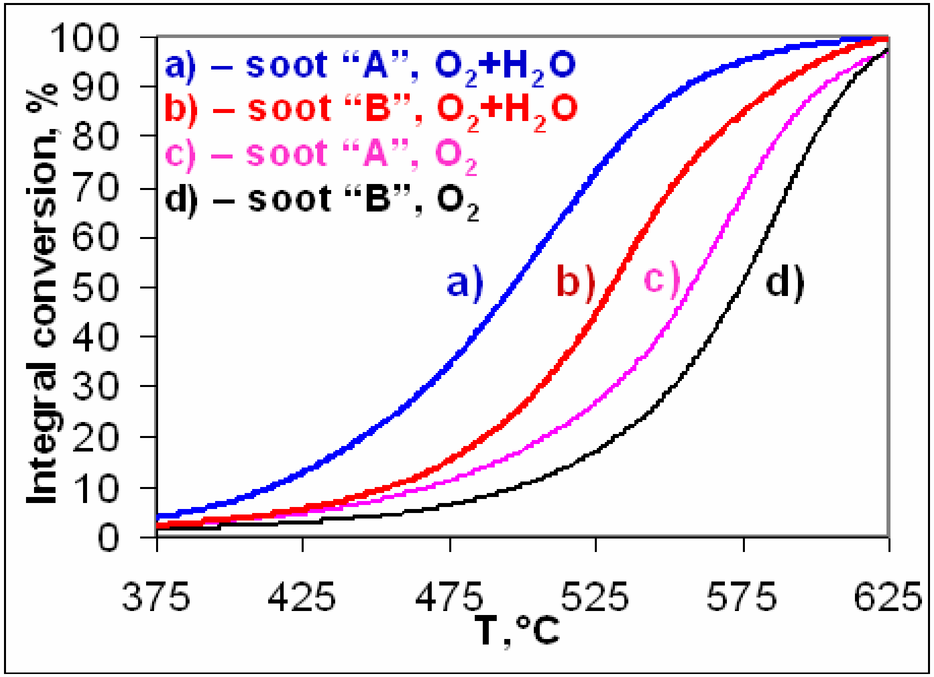
A. Reactivity evolution with progressive oxidation:

– Chemical and/or morphological changes?

B. Soot origin:

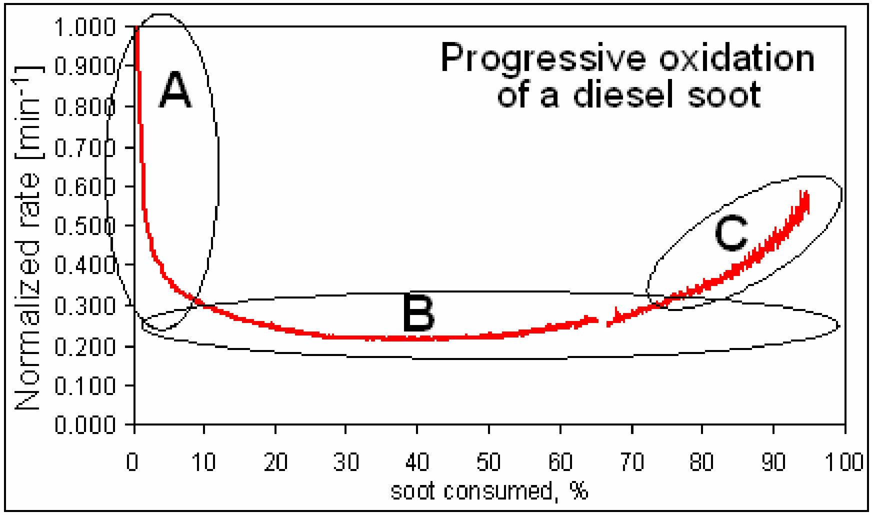
- Large differences between different diesel soot samples
- Structure - reactivity understanding is only evolving[1,2]
  – New combustion recipes may yield soot with unconventional structure[3]

Example: reactivity difference between diesel soot samples [4]



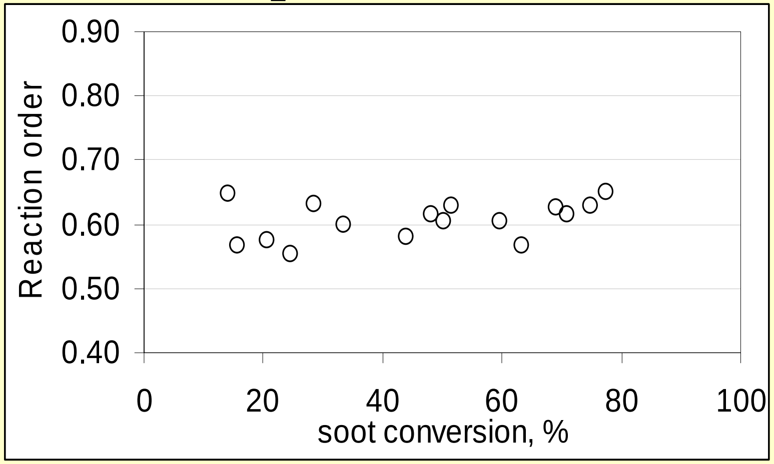
[1,2] R.Vander Wal and A.Tomasek. Combustion and Flame, v134 (2003) p1 & v.136 (2004) p140
[3] D.S. Su et al., Catalysis Today 90 (2004) 127–132
[4] A. Yezerets,N. Currier,H. Eadler,S.Popuri,A.Suresh. SAE 2002-01-1684

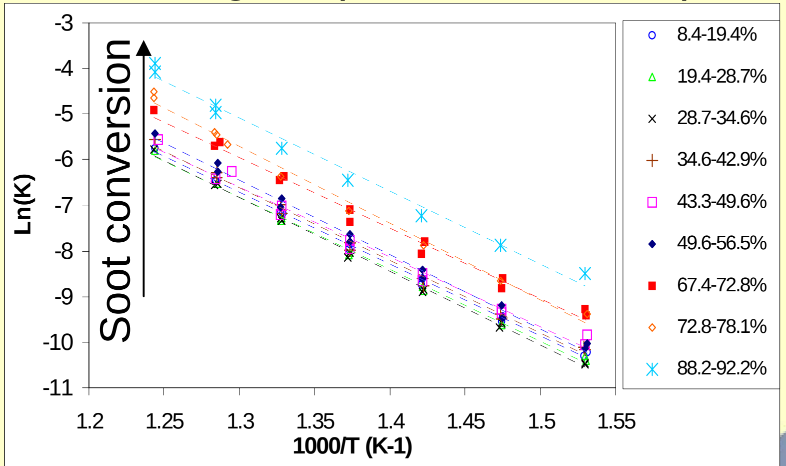
Reactivity Evolution with Progressive Soot Oxidation



- **A**: High reactivity due to:
  - SOF and "Initial high reactivity effect due to ambient aging[1]
- **B:** "steady-state" oxidation
  - Simple Arrhenius kinetics
  - Minimal effect of soot "age"
- **C:** increased reactivity at later stages of oxidation
  - Number of reactive sites per unit weight is increasing?

Effect of $[O_2]$ and temperature at different soot "ages" (soot conversion)

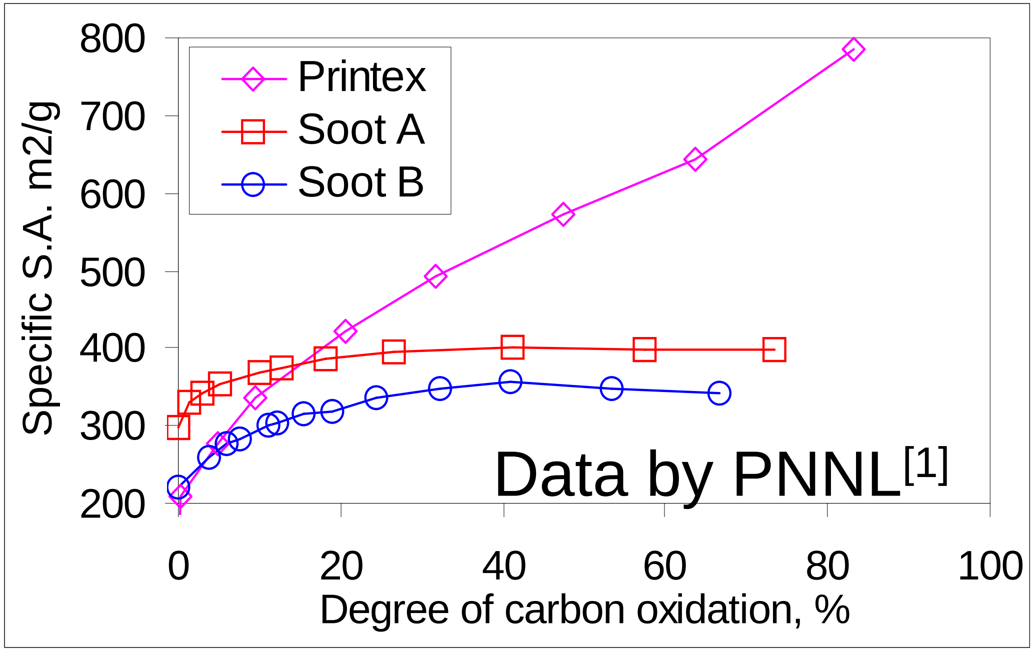




[1] A.Yezerets et al. Catalysis Today Vol. 88 (1-2), pp. 17-25, 20

Reactivity evolution with progressive soot oxidation

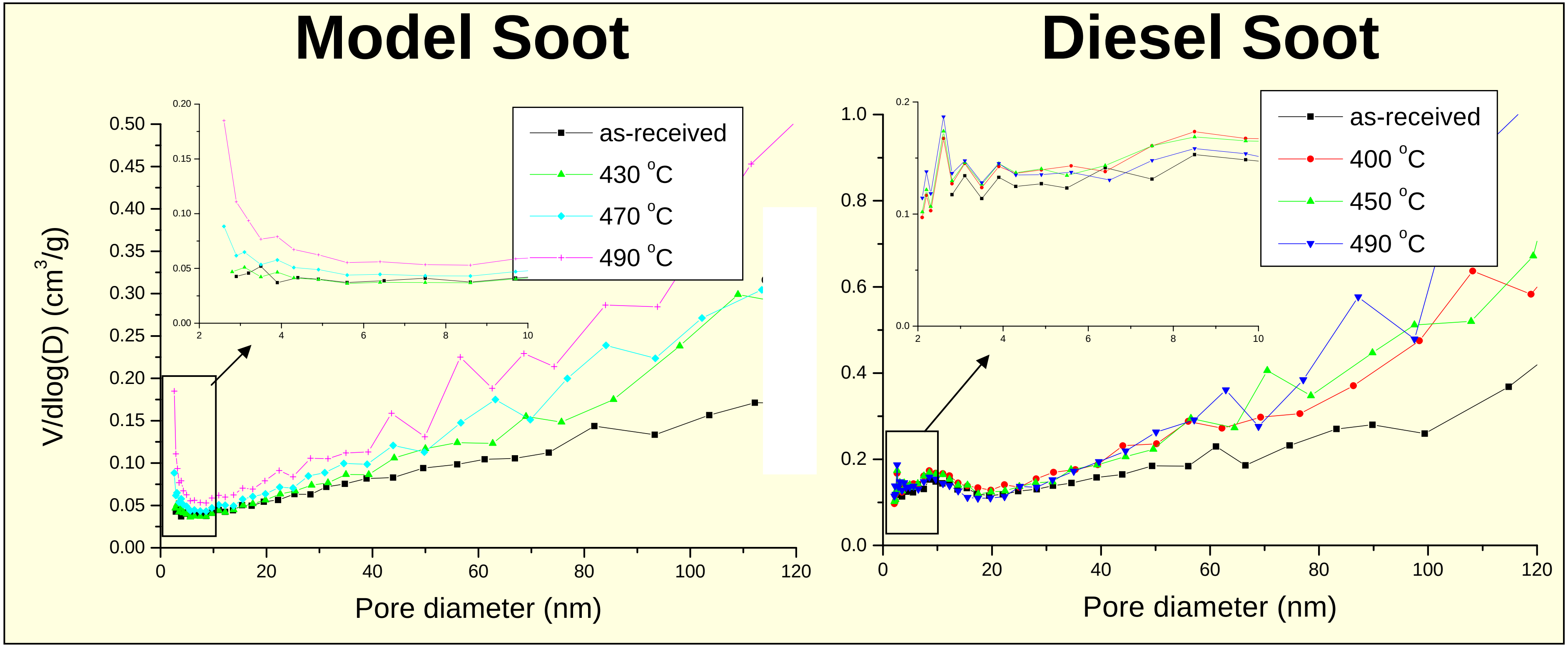
- Reaction ***chemistry*** appears to be independent of the degree of carbon oxidation:
  - No systematic changes in the key kinetic parameters
- ***Density*** of the reactive sites appears to be changing
  - Not accounted by the changes in the BET surface area[1]
- Substantial *qualitative* differences between soot samples
  - Why?



[1] A. Yezerets, D. H.Kim et al. Applied catalysis B: 61 (2005), 134-143.

Further Characterization Work at PNNL

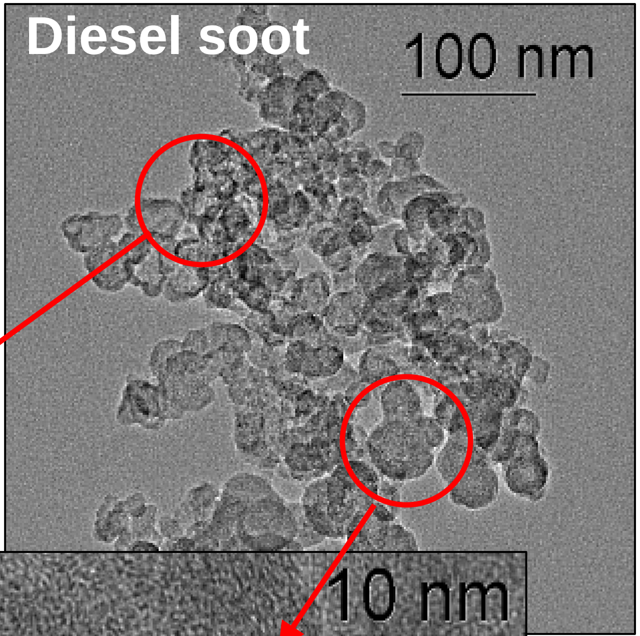
- Porosity Measurements

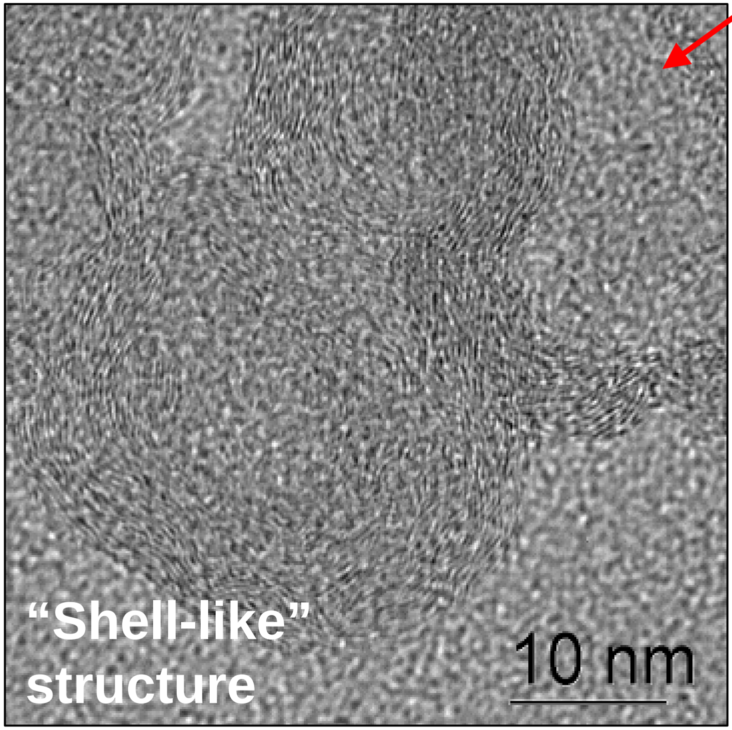


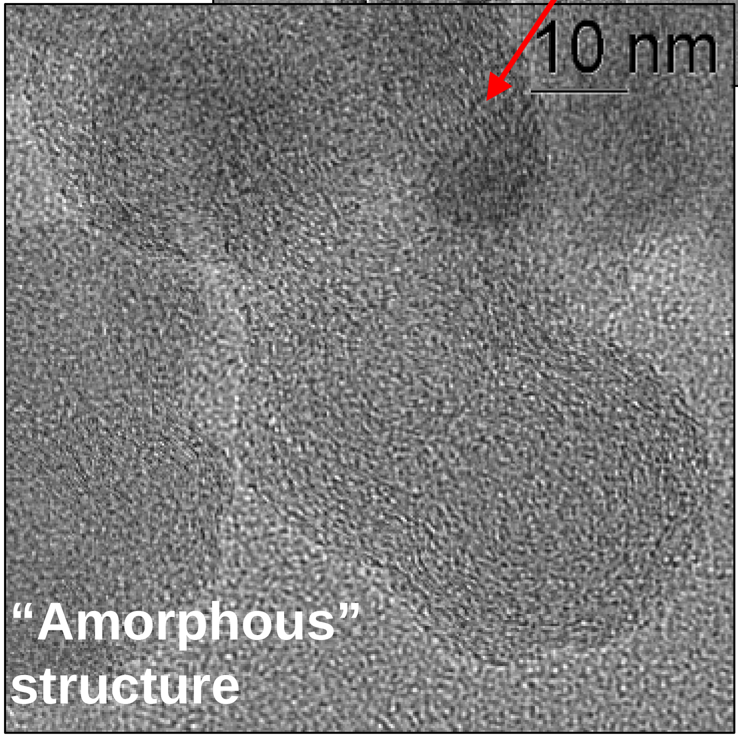
- Model soot: drastic development of the micropores, less than 2 nm.
- Diesel soot: no such trend

Further Characterization Work at PNNL

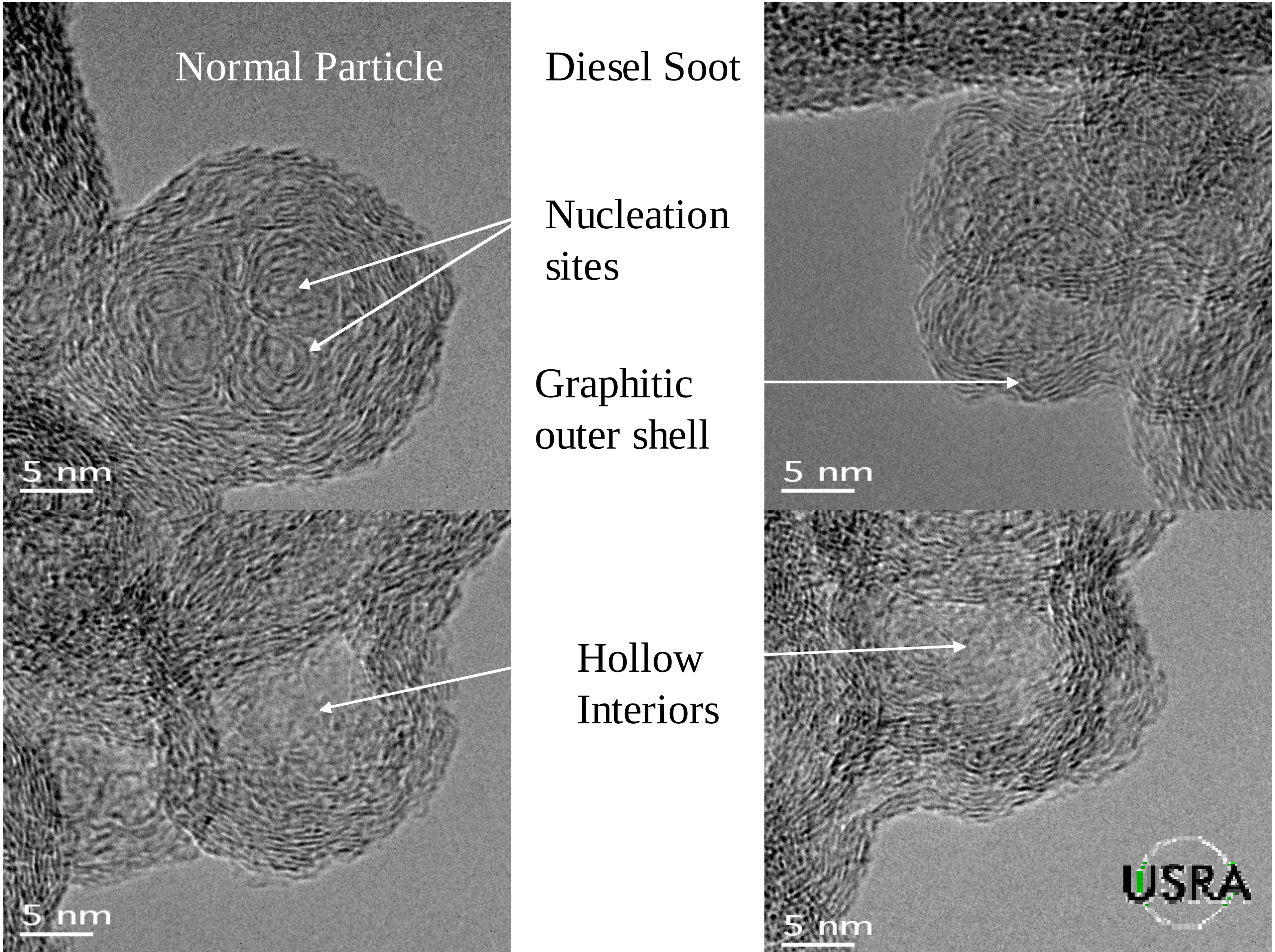
- High-Resolution Transmission Electron Microscopy:
  - Particles with different fundamental structures co-exist in diesel soot
    - Appears to be a a strong function of oxidation conditions



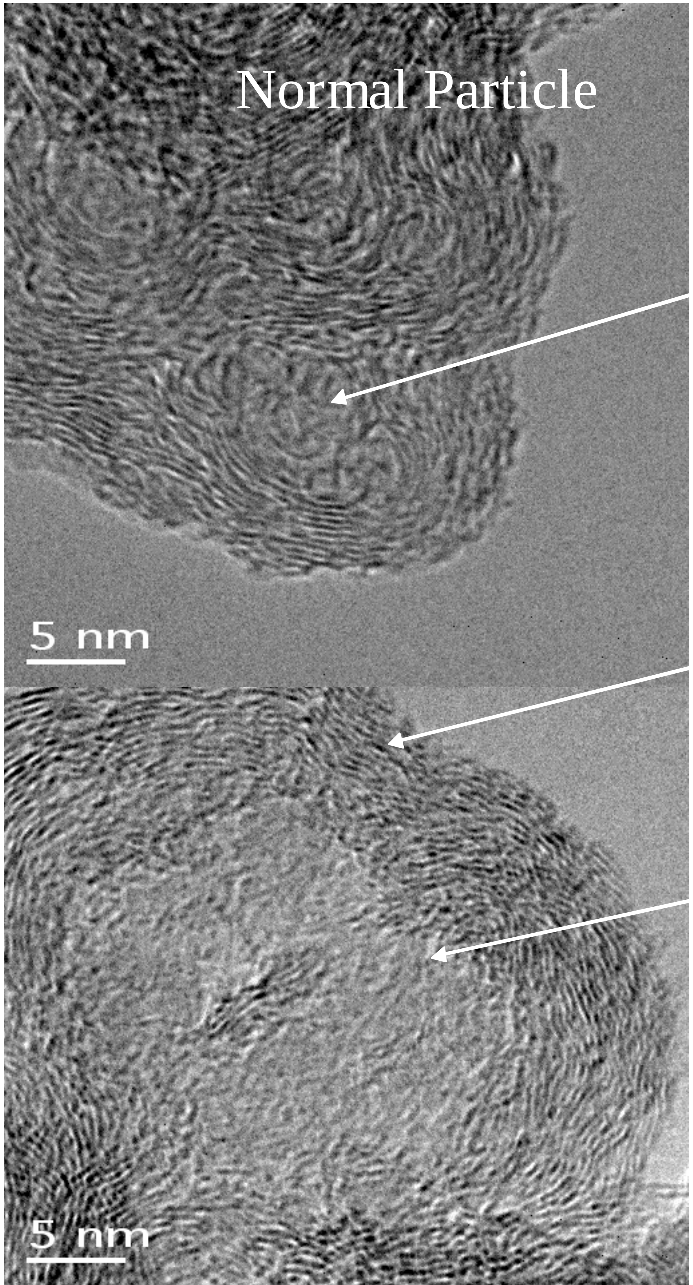




Characterization Work - USRA at NASA-Glenn



Characterization Work - USRA at NASA-Glenn

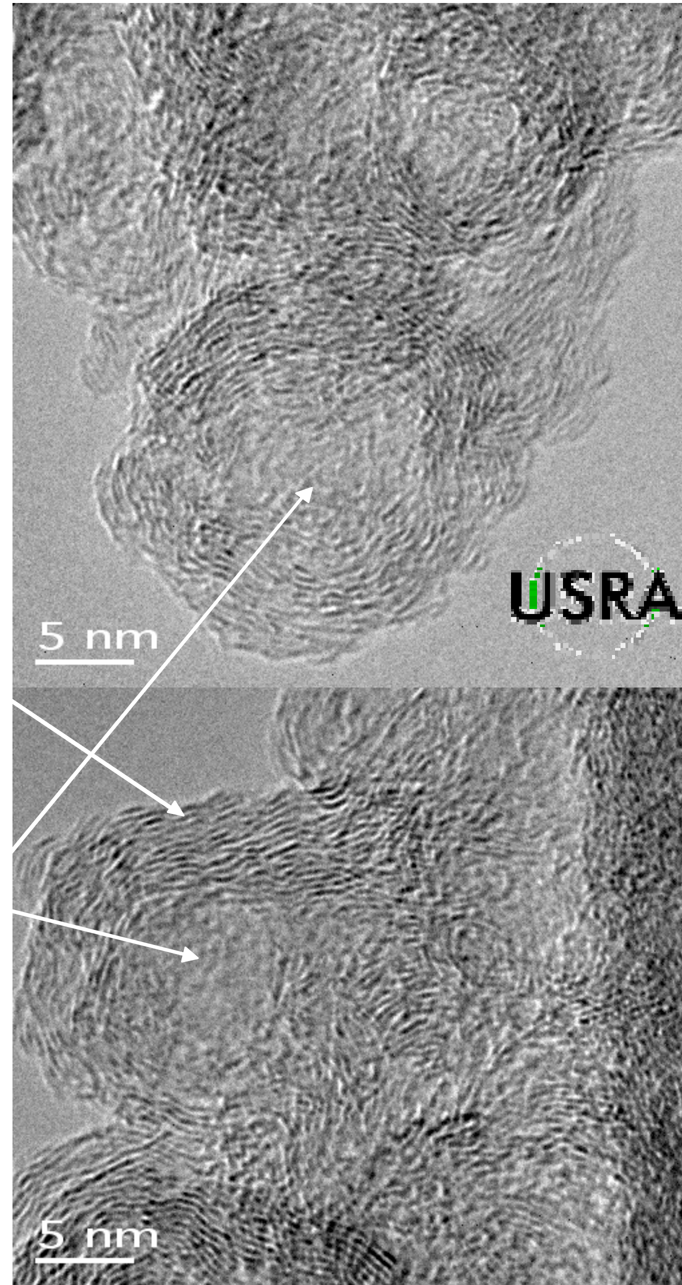


Diesel Soot

Nucleation sites

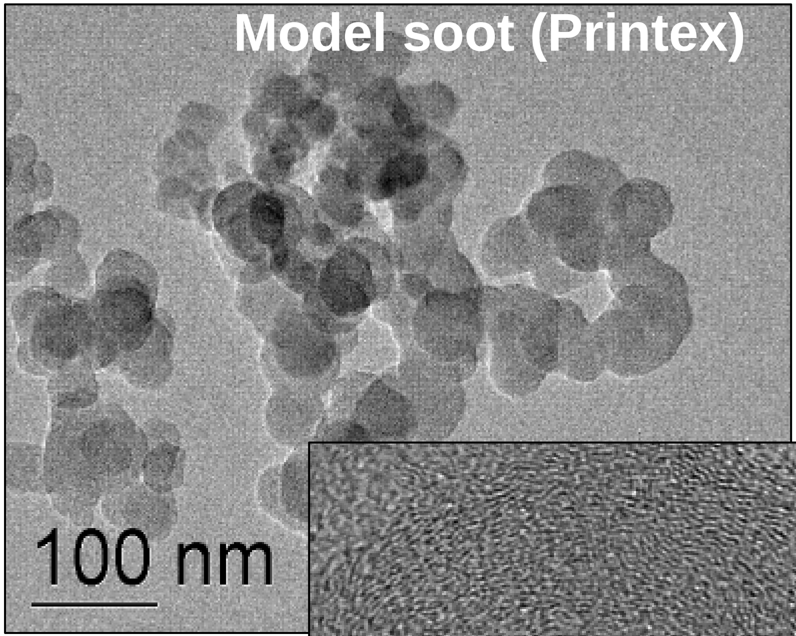
Graphitic outer shell

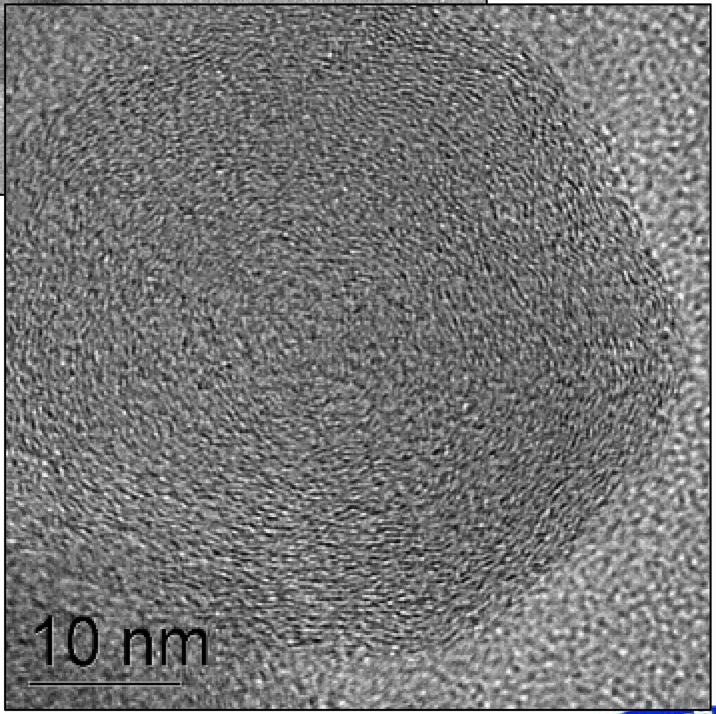
Hollow Interiors



Further Characterization Work at PNNL

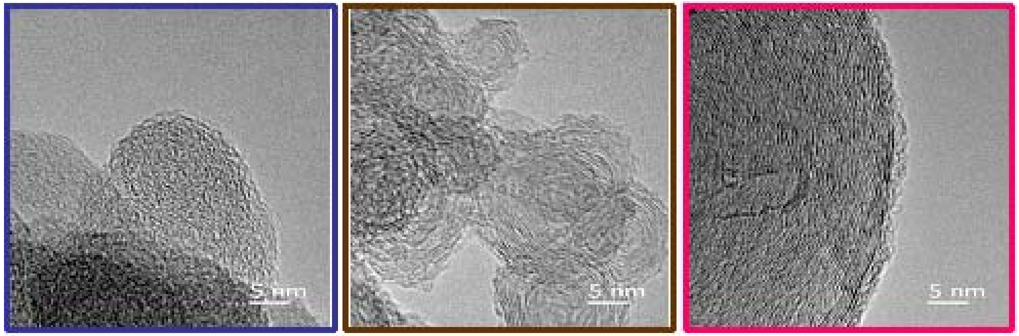
- High-Resolution Transmission Electron Microscopy:
  - *Model soot* sample only contains particles of one type – “amorphous”





- Further TEM Study is underway
  - PNNL
  - USRA at NASA-Glenn
- Additional measurements at PNNL:
  - Raman; ^{13}C and ^{1}H-NMR

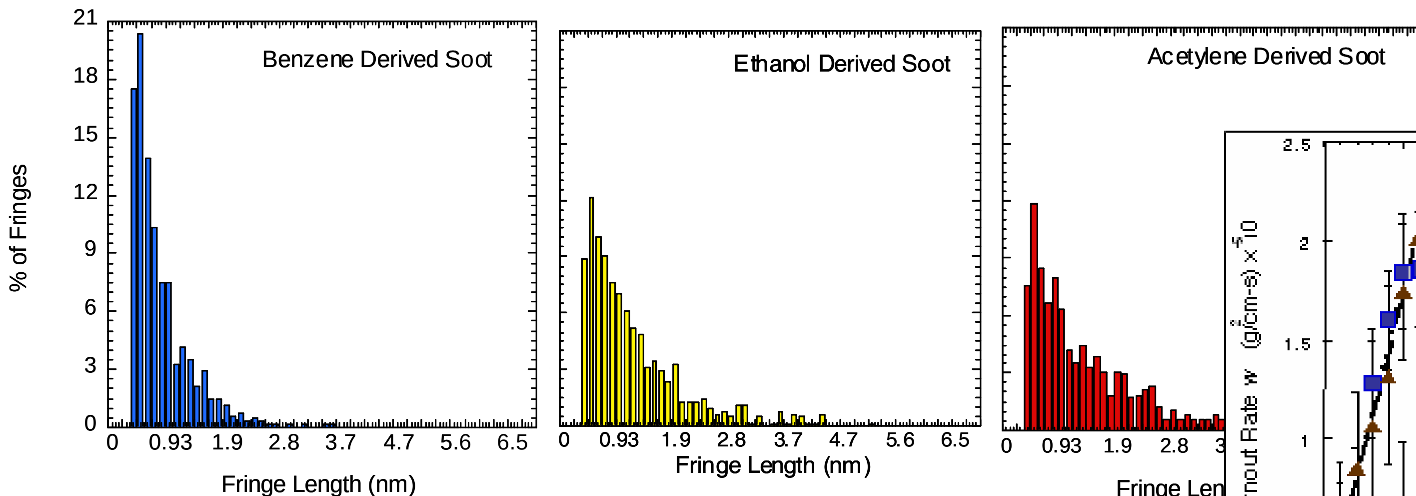
Quantitative description of soot nano-structure

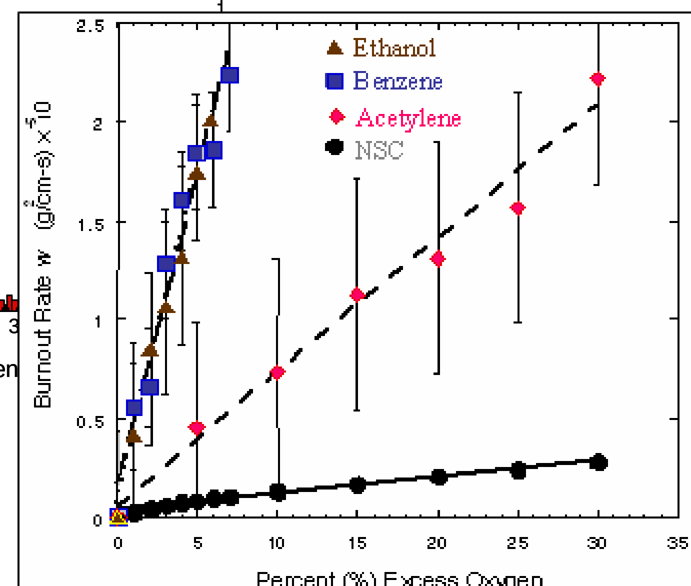


Amorphous Fullerenic Graphitic

Initial work at USRA/NASA:

1) How to *quantify* soot structure?
2) How to correlate nano-structure to the reactivity?





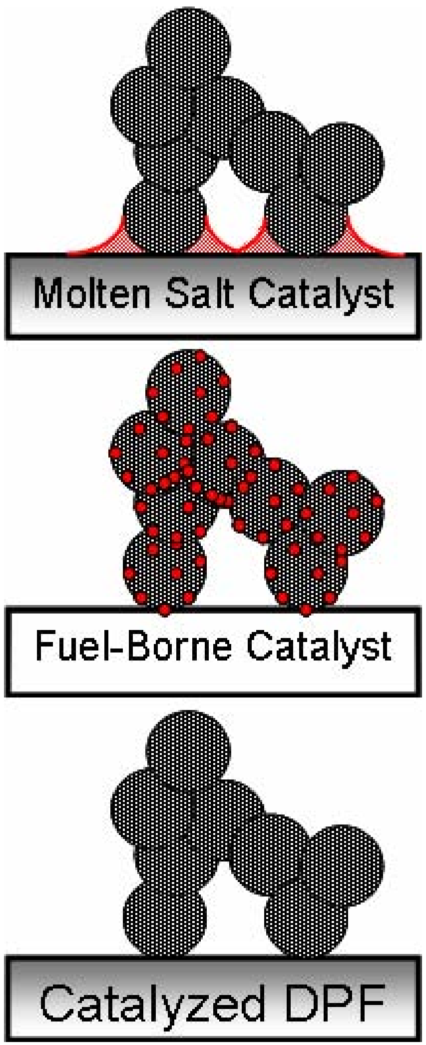
3) How the evolving combustion recipes affect structure and properties of soot?

[1] R Vander Wal and A. Tomasek. "Combustion and Flame 134 (2003) 1–9

III. Catalyst impact on soot oxidation

Clear promotional effect:

- Highly mobile catalysts, e.g. molten salts[1,2]
  - Substrate durability and secondary emissions concerns
- Catalyst incorporated into soot particles
  - Fuel-borne catalysts



Effect of the DPF catalytic coating:

- *Oxidation by* O_2:
  - Is the soot-catalyst contact sufficient to promote oxidation?
    - How does it evolve with the oxidation?
- *Oxidation by* NO_2:
  - Catalyst contribution to the NOx “recycle”?

[1] B.A.A.L. van Setten, R. van Dijk, S.J.Jelles, M.Makkee and J.A.Moulijn. Appl.Cat.B: Env., 21(1) 1999, p51.
[2] B.A.A.L. van Setten, C.G.M.Spitters, J.Bremmer, A.M.M.Mulders, M.Makkee and J.A.Moulijn. Appl. Cat. B: Env., 42(4), 2003, p.337

Evaluation of the Catalyst Effects

- Soot/catalyst contact and its evolution with oxidation
- Heat evolution / dissipation
  - Key for predicting thermal runaway failures
- Flow distribution

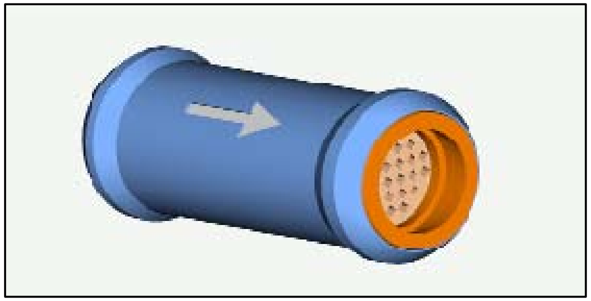
Cummins pilot-rig for soot oxidation:

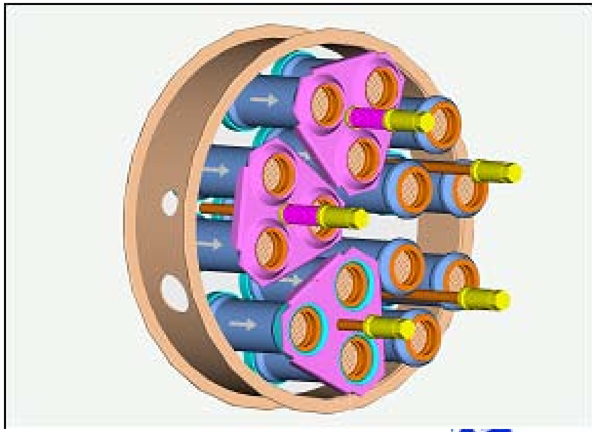
<u>On-engine loading</u>

- Real soot filter cores
- Real soot loaded on-engine

<u>Controlled Bench Regeneration</u>

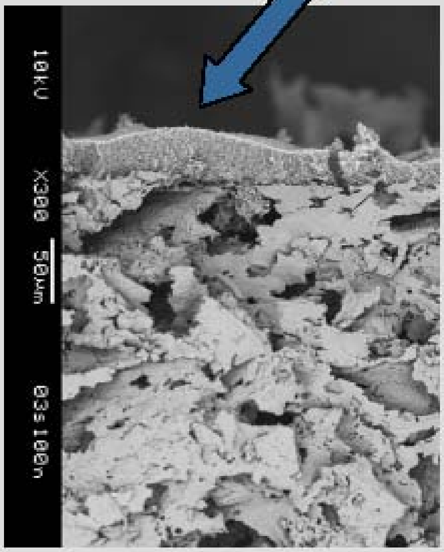
- Detailed ***gas analysis***
- Real-time ***pressure drop***
- Sample ***weighed*** before and after regeneration – mass balance





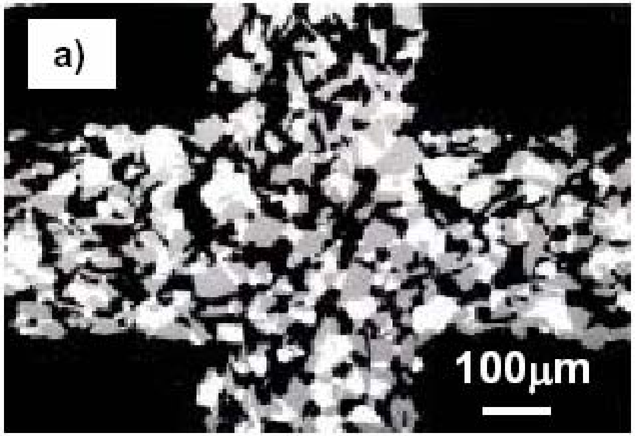
IV. Soot Deposition Topology

- Soot / catalyst contact geometry
  - Changes in soot cake morphology and evolution of soot / catalyst contact with the oxidation
- Back-diffusion of NO_2
- Different substrate materials
  - Different filtration modes

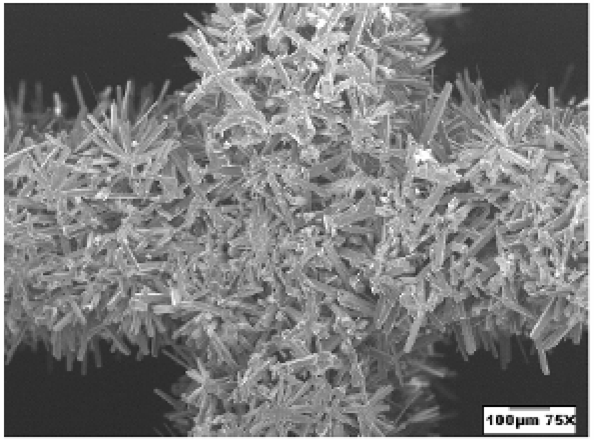


Courtesy of PNNL

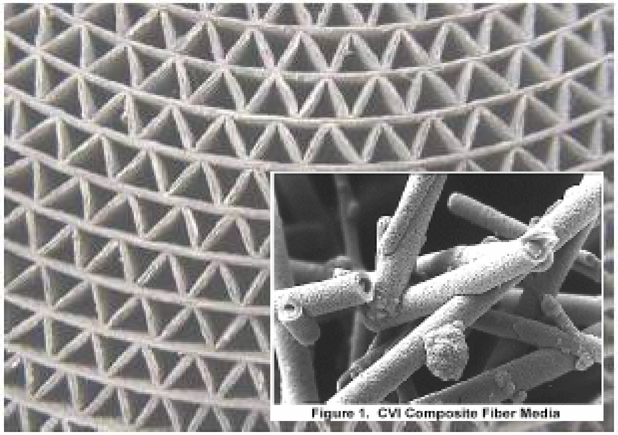
Si-bound SiC
SAE 2004-01-0951



Mullite Substrate (Dow)
SAE 2004-01-0955



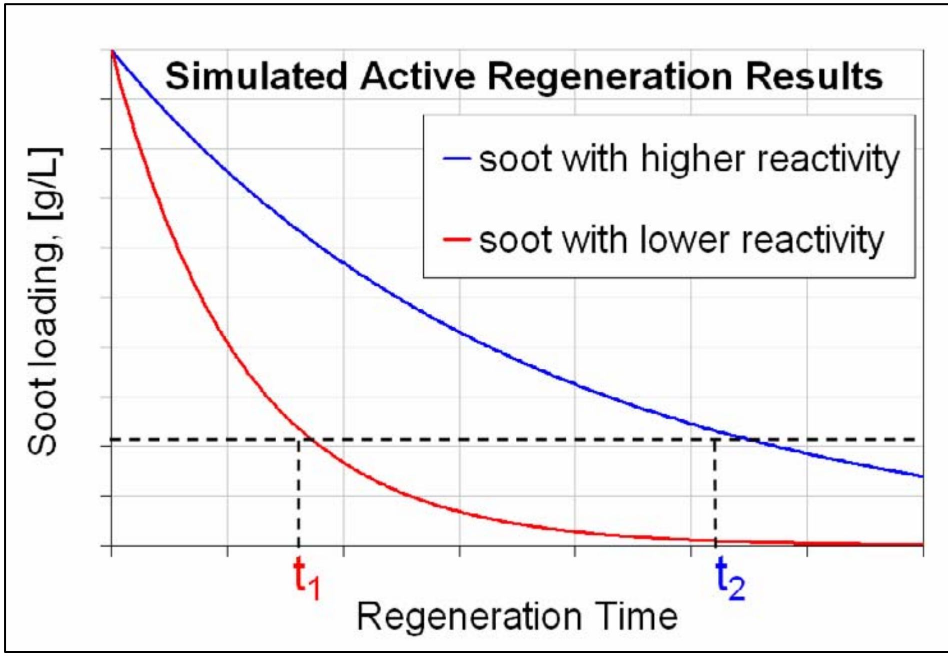
Composite Media (3M)
SAE 2002-01-0323



Quantitative understanding of the soot oxidation offers opportunities for optimizing DPF applications

– Fuel-efficient control strategies

- Soot oxidation can be described by simple algebraic equations, easily handled by the engine ECM
- Virtual soot sensors may provide improved regen. triggers, adjustable to soot reactivity



– Minimized risk of uncontrolled regeneration

- Thermal runaway can be predicted using the developed soot oxidation kinetics, combined with proper, substrate- and soot-deposit-specific, heat transport description.
- Safe soot loading limits can be expanded

Acknowledgments

- Cummins:
  - US DOE, Office of FreedomCar and Vehicle Technologies
- PNNL:
  - US DOE, Office of FreedomCar and Vehicle Technologies.
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